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FINAL REPORT

EXPLORATORY HIGH PRESSURE CHEMISTRY

JOHN A. GLADYSZ

AFOSR-79-0092

UNIVERSITY OF CALIFORNIA, LOS ANGELES
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A novel 1,3-silatropic shift was observed in the acylation of a silylated iron anion. A high yield cycloaddition of allyl iron complexes to olefins under pressure was carried out. This reaction constitutes a relatively rare example of a 3 plus 2 cycloaddition to give a 5-membered carbocyclic ring. It was found that migratory insertion reactions of transition metal alkyls can be effected by the application of pressure.

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FINAL TECHNICAL REPORT

April 1, 1979 - March 31, 1982

Grant AFOSR - 79-0092

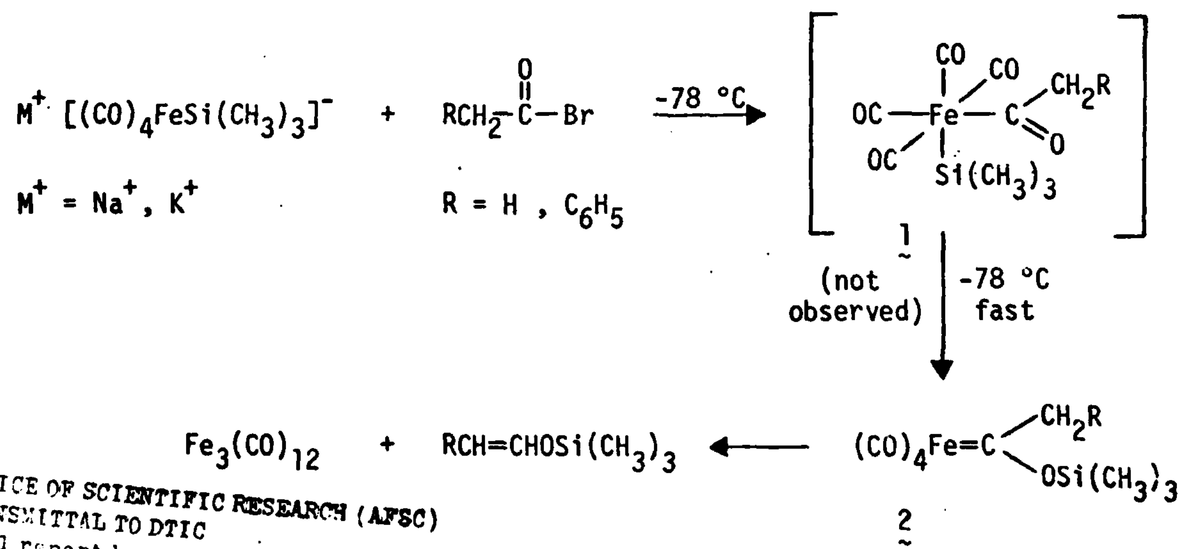
J.A. Gladysz
Principal Investigator
Department of Chemistry
UCLA

Most of the research described in this report deals with high pressure organic and organometallic chemistry. However, due to some difficulties encountered in pursuing this line of research (caused in part by the deaths of two key collaborators, Professors William F. Libby and George Kennedy, during the course of this project; they furnished the host laboratory), the scope of the project was expanded (following consultation with Dr. Matuszko) to include studies of organosilicon and metal/silicon compounds.

I. 1,3-Silatropic Shifts from Iron to Acyl Oxygen

We have completed a study of the acylation of the silylated iron anion $M^+ [(CO)_4FeSi(CH_3)_3]^-$ ($M^+ = Na^+, K^+$).[1] We anticipated formation of acyl intermediates **1** (eq i), and hoped that **1** might eliminate an acyl silane. However, **1** did not prove detectable at -78 °C. Instead, a novel 1,3-silatropic shift occurred to give the carbenes $(CO)_4Fe{=}C(R)OSi(CH_3)_3$ **2**. These have been characterized by ^1H NMR, ^{13}C NMR, and IR. Upon standing at 25 °C, they convert (via a hydride shift) to silyl enol ethers. This work is being submitted to *Organometallics* for publication.

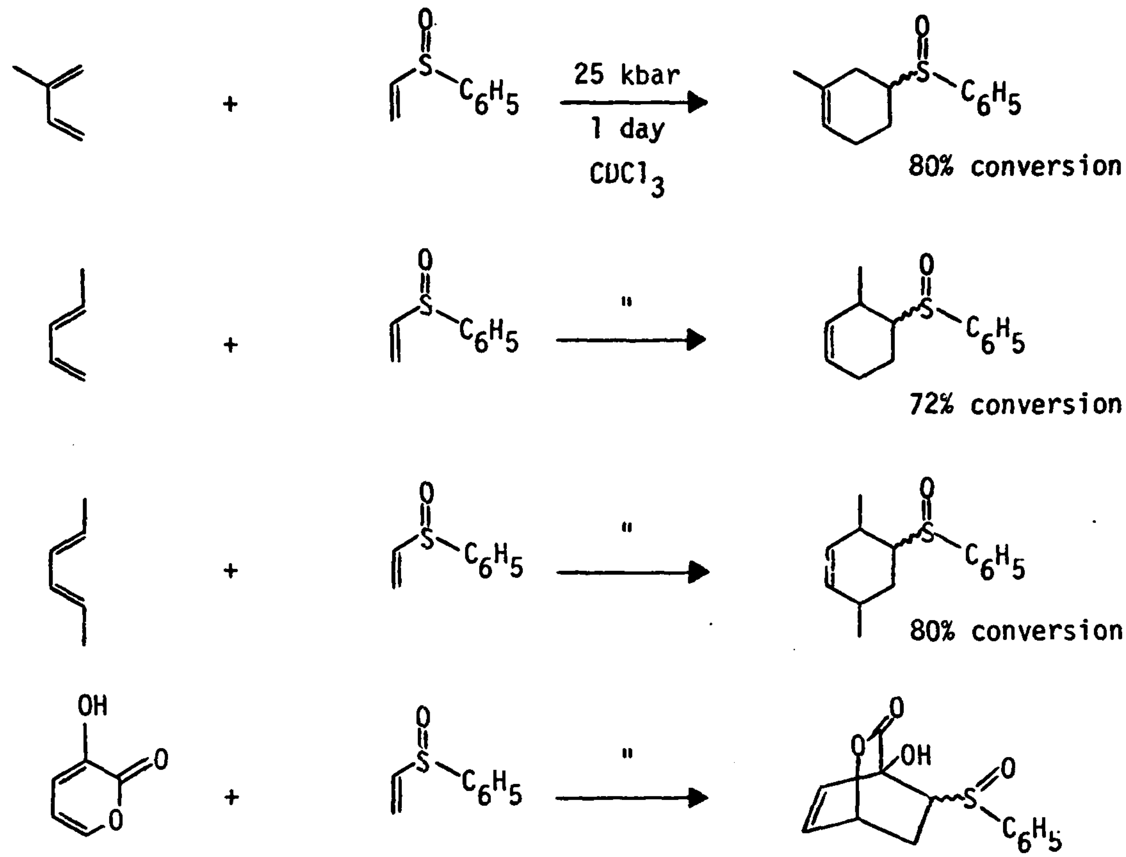
(i)



II. Vinyl Sulfoxide Cycloadditions

We have successfully executed the following cycloadditions of phenyl vinyl sulfoxide:

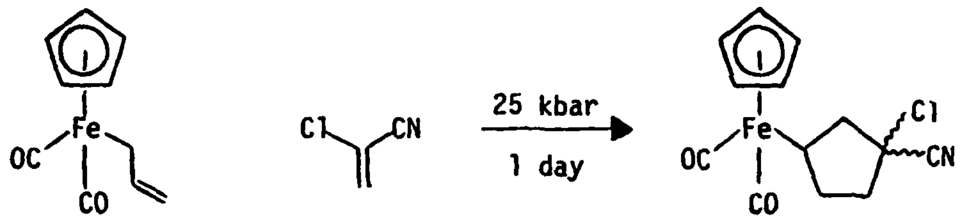
(ii)
(iii)
(iv)
(v)



Normally cycloadditions of phenyl vinyl sulfoxide require such high temperatures that extrusion of C_6H_5SOH (and concommitant olefin formation) occurs.[2] In the above reactions, the sulfoxide group is retained, which provides a convenient handle for carbon-carbon bond forming reactions and other functionality transformations. The products in eq iii-v are obtained as diastereomer mixtures; upon heating, C_6H_5SOH eliminates and previously synthesized[2] dienes form.

III. Cycloadditions of Iron Complexes

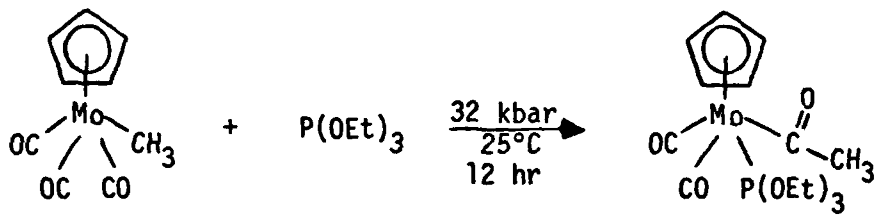
We have been able to effect the high yield cycloaddition of allyl iron complexes to olefins under pressure, as shown in eq vi. This type of cyclopentane forming reaction was previously possible only with the highly electron deficient diene TCNE.[3] We have also been able to execute similar cycloadditions with acrylonitrile and α-(phenylthio)acrylonitrile. This reaction constitutes a relatively rare example of 3+2 cycloaddition to give a 5-membered <u>carbocyclic</u> ring.

(vi) 

(mixture of diastereomers)

IV. "<u>Migratory Insertion</u>" Reactions

We have found that "migratory insertion" reactions of transition metal alkyls can be effected by the application of pressure:

(vii) 

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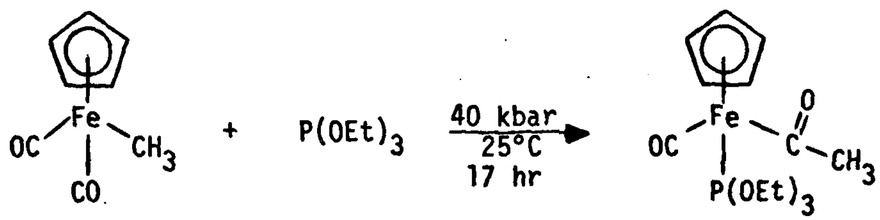
3 4

(viii) 

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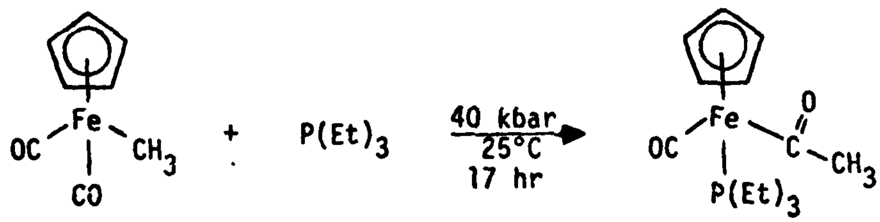
(ix) 

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5 7

Literature conditions for reactions vii-ix indicate that temperatures of 80-120 °C are required[4] at 1 atm. However, our control reactions gave the following results:

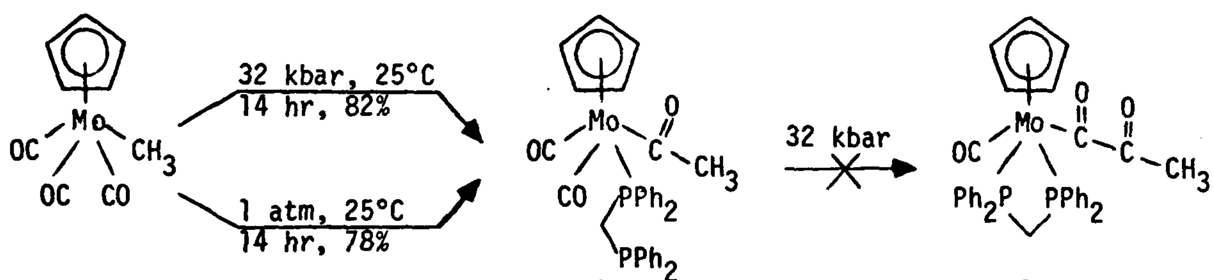
$$\text{(x)} \qquad \mathbf{3} \xrightarrow[\substack{25\ ^\circ\text{C} \\ 12\ \text{hr}}]{1\ \text{atm}} \mathbf{4} \qquad 66\%$$

(compare eq vii)

$$\text{(xi)} \qquad \mathbf{5} \xrightarrow[\substack{60\ ^\circ\text{C} \\ 18\ \text{hr}}]{1\ \text{atm}} \mathbf{6} \qquad 28\%$$

(compare eq viii)

Thus, in a preparative sense, pressure only mildly accelerates rates of "migratory insertions" of transition metal alkyls. Hence $\Delta V^{\ddagger}$ is probably only slightly negative. We attempted to achieve a "multiple" insertion with 3 and $Ph_2PCH_2PPh_2$; however, the target molecule 9 was not obtained, and the thermal, 1 atm reaction yielded identical results (eq xii).

(xii) 

3 8 9

V. Uranium - Silicon Compounds

Compounds with uranium-silicon bonds have not previously been prepared. These may have useful properties for uranium isotope separation, so we have embarked upon some exploratory studies. We have attempted to use the zirconium silane 10 (eq xiii), the synthesis of which we have recently reported,[5] as a trimethylsilyl transfer agent:

$$\text{(xiii)} \quad \tfrac{1}{2}(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2 \;+\; (\eta\text{-}C_5H_5)_3UCl \xrightarrow{?} \tfrac{1}{2}(\eta\text{-}C_5H_5)_2ZrCl_2 \;+\; (\eta\text{-}C_5H_5)_3USi(CH_3)_3$$

$$\underset{\sim\sim}{10} \qquad\qquad \underset{\sim\sim}{11}$$

$$KSi(CH_3)_3 \;+\; (\eta\text{-}C_5H_5)_3UCl \xrightarrow{?} \underset{\sim\sim}{11}$$

When the starting materials in eq xiii are mixed and heated, the dichloride $(\eta\text{-}C_5H_5)_2ZrCl_2$ does form (^1H NMR assay). However, we have not been able to detect the hoped-for U-Si product 11, which is expected to be paramagnetic. A more promising route to 11 appears to be the reaction of $(\eta\text{-}C_5H_5)_3UCl$ with $KSi(CH_3)_3$.[6] A red solid (with a green supernate) forms immediately. Uranium alkyls $(\eta\text{-}C_5H_5)_3UR$ are red.[7] The red solid dissolves in $CH_3OCH_2CH_2OCH_3$ to give a green solution. We are presently attempting to characterize this (apparently paramagnetic) material by NMR (^1H NMR, δ: 1.89, -13.4; 9:15) and ESR. This portion of the project will be continuing through 6/30/82, at which time the principal investigator will move his laboratories from UCLA to the University of Utah.

VI. Other Studies

A. Attempts to add dienes to isonitriles in a 4 + 1 fashion were unsuccessful. This would have been a valuable new (symmetry-allowed) synthesis of 5-membered rings, but diene/diene reactions were faster than diene/isonitrile reactions.

B. Attempts to effect high pressure: (a) RNO_2/olefin 2 + 3 cycloadditions; (b) triquinacene reactions; (c) Homo-Diels-Alder reactions; (d) allyl silane reactions; (e) silacyclopentadiene (silole) cycloadditions; (f) sulfide alkylations; (g) Kornblum oxidations (with DMSO) were unsuccessful.

C. Several attempts to make π-silacyclopentadienide complexes by cocondensation of iron atoms with silacyclopentadienes (siloles) were unsuccessful.

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(2) "Ene Reactions of β-Pinene at Room Temperature and 40 kbar Pressure," J.A. Gladysz and Y.S. Yu, J. Chem. Soc., Chem. Commun., 599 (1978).

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(4) "Alkylation and Acylation of the $[(CO)_4FeSi(CH_3)_3]^-$ Anion; A Novel 1,3-Sigmatropic Shift from Iron to Acyl Oxygen," A.J. Blakeney, W. Krone-Schmidt, and J.A. Gladysz, in preparation for Organometallics.

Public Lectures Based Upon This Project

(1) University of Idaho, Moscow, Idaho, "Organic Reactions Under Extreme Conditions: From Hot Atoms to 50,000 Atmospheres," April 19, 1979.

(2) G.D. Searle & Co., Chicago, Illinois, "I. Synthetic Chemistry under 20-40 Kbar Pressure; II. New Methods of Asymmetric Organic Synthesis; 100% Chirality Transfer from Rhenium to Carbon," March 28, 1980.

(3) Exxon Research and Engineering, Linden, New Jersey, "Organic Reactions Under Extreme Conditions: From Hot Atoms to 50,000 Atmospheres," March 1, 1982.

(4) 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Canada, "Organic Chemistry Under Extreme Conditions: Hot Atoms to 50,000 Atmospheres," August 18, 1981.

Coworkers On This Project

(1) Postdoctoral: Dr. Bong-Rae Cho

(2) Graduate Student: Mr. Wilfried Krone-Schmidt
A portion of Wilfried's Ph.D. thesis will be based upon this project.

(3) Undergraduate Students: Mr. David Parker
Mr. Ron Ugolick
Mr. Yeung Yu
Mr. Jim Tomasello
Mr. Sung Lee